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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The work carried out under this contract was concerned primarily with attempts to synthesize dinitroacetylene. Only two nitroacetylenes have as yet been reported, namely isopropyl- and t-butyl-nitroacetylene, both of which were made originally by elimination of hydrogen halide from suitable precursors under rather drastic conditions. A subsidiary objective of this work was to develop new methods for preparing nitroacetylenes in general. While neither objective has been attained, the results reported here seem to have led to a better understanding of the problems involved.		

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DINITROACETYLENE AND RELATED COMPOUNDS

FINAL REPORT

APRIL 20, 1983

DAAG29-81-K-0008

THE UNIVERSITY OF TEXAS

AUSTIN, TEXAS

83 06 01 02

PEOPLE SUPPORTED BY THIS GRANT

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Charles Reynolds

DEGREES EARNED

James P. Ritchie , PhD.

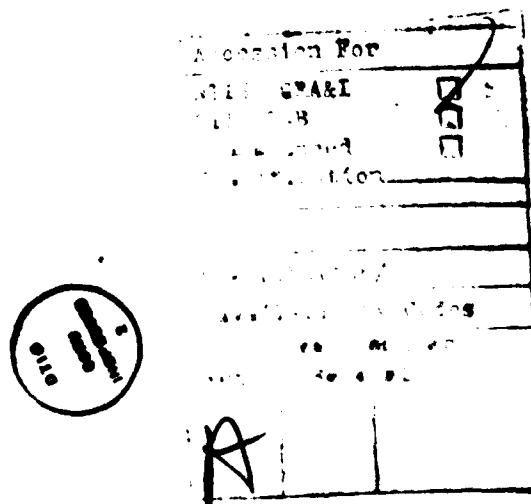
Dissertation Title: A Molecular Orbital Study of the Ozonolysis
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The following manuscript submitted for publication:

GROUND STATES OF MOLECULES. 65. THERMOLYSIS OF MOLECULES
CONTAINING NO₂ GROUPS.

Authors: Michael J. S. Dewar and James P. Ritchie



83 06 01 029

FINAL REPORT

The original incentive for this work came from a prediction by Dr. J. Alster, at Picatinny Arsenal, that octanitrocubane (1a) might be the "ultimate" conventional explosive. Since the only practical route to 1a seemed to be by tetramerization of dinitroacetylene (2), following the preparation¹ of the known octakis-trifluoromethyl cubane (1b) from 1,1,1,4,4-hexafluoro-2-butyne, and since 2 also seemed likely to be of major interest in its own right, both an intermediate in synthesis and as a phenomenally powerful electron acceptor, the preparation of 2 seemed a very worthwhile goal.

The work carried out under this contract was concerned primarily with attempts to synthesize this hitherto unknown species. Indeed, only two nitroacetylenes have as yet been reported², namely isopropyl (3a) and t-butyl (3b) nitroacetylene, both of which were made originally by elimination of hydrogen halide from suitable precursors under rather drastic conditions. A subsidiary objective of our work was to develop new methods for preparing nitroacetylenes in general. While neither objective has been attained, the results reported here seem to have led to a better understanding of the problems involved, in particular the conditions that must be met in any practical synthesis of 1.

Attempts to Prepare Nitroacetylenes by Elimination Reactions

Our first experiments were based on the route used² to make 3, i.e. elimination of hydrogen halide from a suitable precursor. As yet, no monochloro derivative of 1,2-dinitroethylene has been reported and 1,2-dinitroethylene (presumably the trans

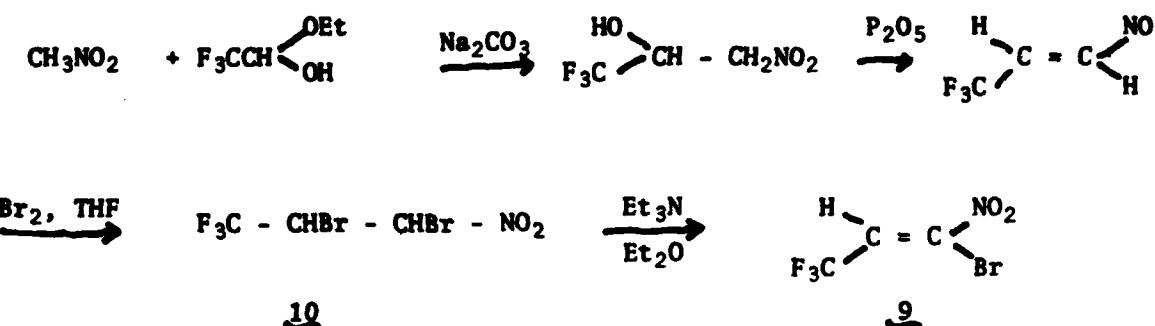
isomer), obtained by oxidation of the corresponding dianion¹, was stated to be rather unstable. We were able to obtain 1,2-dichloro-1,2-dinitroethane by addition of dinitrogen tetroxide to 1,2-dichloroethylene but only in low yield at very low conversions. Longer reaction times or use of higher temperatures led to the formation of oxalic acid. Attempts to make 1,2-dibromo-1,2-dinitroethane from 1,2-dibromoethylene in a similar way gave only a mixture of trans (5;72%) and cis (6;16%) 1-bromo-2-nitroethylene. Presumably the intermediate radical loses a bromine atom more easily than it adds NO₂; i.e.



Attempts to dehydrobrominate 5 to nitroacetylene using a variety of bases, including diazabicyclononene, gave unreacted starting material.

Attempts were then made to prepare 1-nitro-3,3,3-trifluoropropyne (7), partly as a model for the synthesis of 1 and partly to study its tetramenization to a cubane, (8), as a model for the conversion of 1 to octanitrocubane (1a). The necessary precursor, cis-1-bromo-trans-1-nitro-3,3,3-trifluoropropene (9) was prepared by the following route via 1,2-dibromo-1-nitro-3,3,3-trifluoropropene (10). Neither 9 nor 10 has been reported previously.

Again, all attempts to dehydrobrominate 9 to 8 failed, the only products being dark red viscous oils with no acetylenic i.r. bands.



The crucial step in elimination of hydrogen halide from positively substituted olefines is clearly the loss of halide ion from an anion (E_{CB}^1 mechanism). The same anion should be formed by reduction of a dihalide by addition of electrons. The necessary precursors for 1 would then be a 1,1,2,2-tetrahalo-1,2-dinitroethane (11). The corresponding tetrachloride (11a) and tetrabromide (11b) can indeed be obtained easily by addition of N_2O_3 to tetrachloroethylene or tetrabromoethylene and we were also able to obtain 1,1,2-trichloro- 1,2-dinitro- 3,3,3-trifluoropropane (12) in a similar way from 1,1,2-trichloro- 3,3,3-trifluoropropene (13).

Extensive attempts were then made to convert those compounds to acetylenes by reduction, but without success.

(1) Both 11a and 11 failed to react with iron pentacarbonyl while 11b gave an unstable product from which nothing definite could be isolated and containing no acetylenic i.r. bands.

(2) Zinc reacted with 12 under a variety of conditions but no definite product could be isolated.

(3) Sodium iodide seemed to react with 11 or 12 but again no product could be isolated from runs under a variety of conditions.

(4) 11b failed to react with copper, a zinc-copper couple, or aluminum. Reaction with triphenylphosphine or trimethyl phosphate in ether gave only unidentifiable tars. Similar results followed from the reaction of 11b with hydrazine or phenylhydrazine.

(5) 11b reacted fairly clearly with magnesium in ether to form tribromonitroethylene (14a), a new compound, in 78% yield. The same product was obtained from reactions of 11b with sodium, lithium, or methyl lithium.

This last result seems very discouraging from the point of view of elimination as a route to 2 because it seems to indicate that elimination of nitrite ion takes place more easily than that of bromide. This route to 2 was therefore abandoned.

Attempts to Prepare 2 by Nitration.

An obvious possible route to nitroacetylenes would be by nitration of a metal acetylidy or an acetylene carrying a substituent capable of easy electrophilic displacement and indeed 3b has been obtained in this way*. However, very extensive studies of the reactions of alkali metal, zinc, cuprous, or silver acetylides, and of acetylenic Grignard reagents, with a variety of nitrating agents, including N_2O_4 , N_2O_5 , CH_3ONO_2 , $NO_2BF_4^-$, NO_2Cl , and C_9NO_2 , all failed to give identifiable products and the tarry material had featureless i.r. spectra indicating that polymerization had taken place. This failure was not unexpected because

nitroacetylenes are very strongly electrophilic and 1 should be exceptionally so. It would therefore be expected to react with an acetylide at least as fast as with the nitrating agent, leading to anionic polymerization.

Attempts were therefore made to nitrate less nucleophilic acetylene derivatives, in particular trimethylsilyl (15) and trimethylstannyl (16) derivatives, ethynyltriphenylphosphonium salts (17), acetylenecarboxylic acids (18) and salts of such acids. The products were again intractible gums with mostly characterless i.r. spectra. In one or two cases weak bands were observed in the acetylenic region but attempts to isolate the products failed. This route was therefore also abandoned and unpromising.

Approaches Involving Reverse Cycloaddition

One procedure which has been used extensively to make otherwise inaccessible unsaturated compounds is reverse cycloaddition, involving pyrolysis of Diels-Alder adducts. A possible route of this kind to 2 seemed to be provided by addition of e.g. dimethyl acetylenedicarboxylate (19) to the known⁹ 2,5-dibromo-3,4-dinitro-thiophene (20) followed by pyrolysis of the adduct. We were, however, unable to persuade 19, or indeed any other acetylene, to add to 20. Since our calculations (see below) had at this point indicated that 2 is unlikely to be stable even at room temperature, implying that any pyrolytic route to it would be doomed to failure, this approach was also abandoned.

Routes via Dinitrosoacetylene

One unique feature of 2 is that the corresponding dinitroso compound (21) is a valence tautomer of cyanogen-bis-N-oxide (22) and should be oxidizable to 2. A standard route to nitrile oxides is the dehydration of nitroparaffins by isocyanates, e.g.

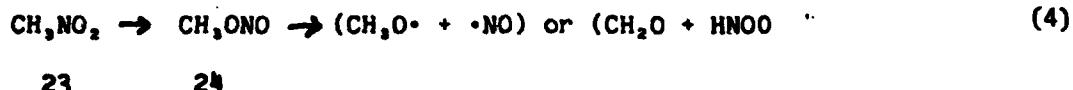


However no identifiable product was formed when 1,2-dinitroethane was treated with phenylisocyanate under various conditions and no adduct was formed when the reactions were carried out in the presence of cyclopentadiene.

Theoretical Calculations

Extensive MINDO/3⁵ calculations⁶ had been previously carried out for the thermal decompositions of methyl nitrate and nitrite, of nitromethane, and of cubane, nitrocubane and 1,2-dinitrocubane. These had indicated that nitro groups exert an unexpected strengthening effect on adjacent CC bonds, the activation energy for CC bond rupture in cubane (the rate-determining step in its thermolysis) being increased by nitro substituents. Preliminary calculations indicated that nitro groups exert similar stabilizing effects in ethylene and acetylene. However, kinetic studies have indicated that the thermolysis of nitromethane (23) does not take place by fission into methyl radicals and nitrogen dioxide because

the observed activation energy is much less than the CN bond strength. Our calculations showed that there is indeed an easier path, involving a preliminary rearrangement of 22 to methyl nitrate (24), which can dissociate readily into radicals ($\text{CH}_3\text{O}\cdot + \cdot\text{NO}$) or by a reverse (2+2) cycloaddition to give $\text{CH}_2\text{O} + \text{HNO}_2$, i.e.



The activation energy for thermolysis of 24 is much smaller than that for the rearrangement, so the latter is the rate-determining step in the thermolysis of 23.

Since the rearrangement of 23 to 24 involves a typical 1,2 migration of methyl and since unsaturated groups usually migrate more easily than saturated ones in such processes, nitroethylenes and nitroacetylenes are likely to decompose via similar rearrangements to nitrites. Table I shows the activation energies calculated by MINDO/3 for several such rearrangements together with heats of reaction for dissociation of the resulting nitrites into alkenoxy or alkynoxy radicals and nitric oxide. It will be seen that nitroethylene and nitroacetylene are indeed predicted to rearrange much more easily than 23 and also that the subsequent fission into radicals should also be much less endothermic, as would be expected in view of their resonance stabilization. Furthermore, the rearrangements are greatly facilitated by β -nitro groups, as again would be expected because resonance structures (e.g. 25) can be written for the transition states with a negative

charge on the β -nitro group.

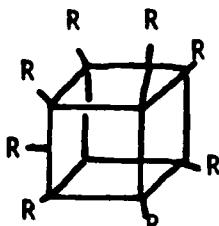
While MINDO/3 calculations are not of course by any means exact, the fact that MINDO/3 reproduces the activation energy for decomposition of 23 closely suggests that the results in Table I are reasonably reliable. It is true that 1,2-dinitroethylene has been isolated³ as a crystalline solid which would imply a larger activation energy for decomposition than our value. However, the latter referred to the cis isomer, which must be destabilized by interactions between the nitro groups, whereas the compound reported is likely to have been the more stable trans isomer. It seems in anycase to have been unstable, surviving only if kept cold.

Our calculations therefore strongly suggest that neither 2 nor tetranitroethylene (26) is likely to exist for any length of time at or above room temperature. Any attempted synthesis of 2 should therefore be carried out at low temperatures or under conditions where it reacts immediately on formation to give some desired product. Similar remarks apply to 26. While this has not yet been reported, its adduct (27) with anthracene has been known for some time. Presumably attempts to prepare 26 by pyrolysis of 27, via a reverse Diels-Alder reaction, failed, as our calculations would lead us to expect.

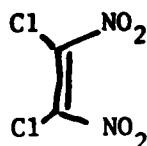
In view of the very large energy release expected in the conversion of 2 to nitrogen and carbon dioxide and the expected facility with which it is likely to undergo explosive decomposition, any attempts to prepare it in the free state should be carried out with extreme caution.

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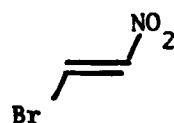
1
a, R=NO₂
b, R=CF₃



4



2



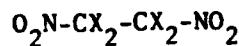
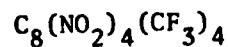
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3



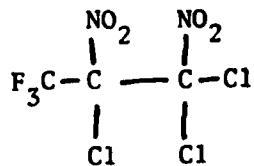
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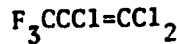
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8

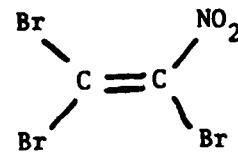
11
a, X=Cl
b, X=Br



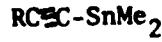
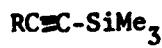
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13



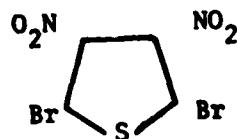
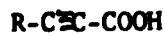
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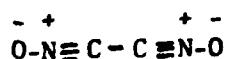
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19

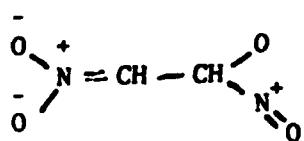
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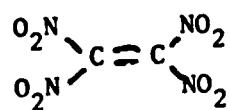
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22



25



26

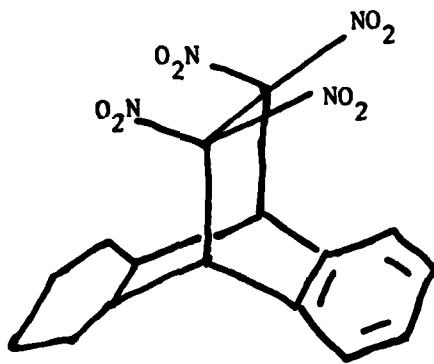
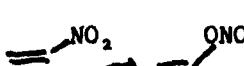
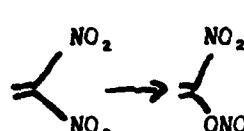
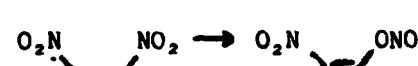
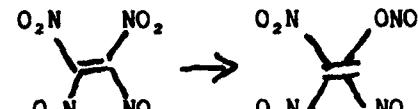


TABLE I. CALCULATED ACTIVATION ENERGIES

REACTION	ACTIVATION ENERGY(KCAL/MOLE)
$\text{CH}_2\text{NO}_2 \rightarrow \text{CH}_3\text{ONO}$	47.0
	33.9
	39.9
$\equiv\text{-NO}_2 \rightarrow \equiv\text{-ONO}$	34.1
	19.9
	21.5
$\text{F}_3\text{C}-\equiv\text{-NO}_2 \rightarrow \text{F}_3\text{C}-\equiv\text{-ONO}$	23.9
$\text{O}_2\text{N}-\equiv\text{-NO}_2 \rightarrow \text{O}_2\text{N}-\equiv\text{-ONO}$	20.0
$\equiv\text{-ONO} \rightarrow \dot{\text{C}}\text{H-CO} + \text{NO}$	16.7
$\text{F}_3\text{C}-\equiv\text{-ONO} \rightarrow \text{F}_3\text{C-C=O} + \text{NO}$	4.2
$\text{O}_2\text{N}-\equiv\text{-ONO} \rightarrow \text{O}_2\text{N-C=C=O} + \text{NO}$	10.7